



# A new method for growing $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ single crystals and investigation of their properties

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## Abstract

Large single crystals of the copper-free  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  (BKBO) superconductor have been successfully grown using modified method of electrochemical deposition. For the first time we employed the method of growth where a  $\text{BaBiO}_3$  single crystal plate was used as a seed. A BKBO layer with (1 0 0) orientation and  $\sim 1$  mm thick grown on the substrate was cut off and thereafter used as a secondary seed. We used a dynamic method, i.e., a crystal holder with reciprocating motion to homogenize the potassium distribution over the crystal volume. The maximum volume of the as-grown crystals reached  $\sim 2 \text{ cm}^3$  with the FWHM of the Bragg reflection curves not exceeding  $1^\circ$ . The lattice structure of the Abrikosov vortices as well as the character of defects of the  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  single crystal, caused by the growth technique, has been studied by small-angle neutron scattering. From SQUID magnetisation measurements, the growth-induced anisotropy of hysteresis loops and pinning force of the second-order superconductor are reported. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Superconductivity in the  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  (BKBO) system was first discovered in ceramic materials

[1,2] and somewhat later in micron-sized single crystals grown by the flux melt method [3]. The BKBO was shown to be a type II superconductor with a superconducting transition temperature  $T_c \sim 30$  K and a simple perovskite structure containing no magnetic ions. One fundamental problem of interest in second-order-type superconductors is the study of the structure of vortices

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lattice and their behaviour in magnetic fields. This problem can be addressed using the small-angle neutron scattering (SANS) technique. Electrochemical deposition from KOH fluxes developed by Norton [4] allowed one to prepare single crystals up to 1 mm<sup>3</sup> in volume. The first BKBO single crystals grown using this method had large mosaic structures and an inhomogeneous distribution of potassium in the crystal volume. Further investigations of electrochemical growth conditions suggested that it is possible to grow more perfect crystals with volumes up to 100 mm<sup>3</sup> [5–11].

In this paper, experimental evidence on the seeded growth of large BKBO single crystals for use in neutron diffraction and other nuclear physics experiments are reported for the first time.

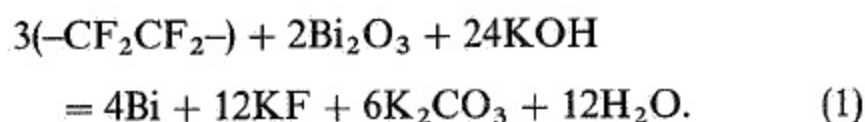
## 2. Experimental results and discussions

### 2.1. Growth method

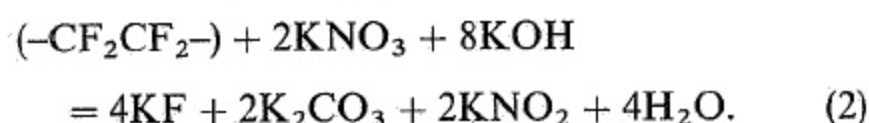
The electrochemical growth of BKBO single crystals was carried out from KOH flux at temperatures of 240–290°C in teflon crucibles with alkali melt volume up to 100 cm<sup>3</sup>. At the first stage of process, BaO (4N) was added to the molten KOH flux to be homogenised until it was completely dissolved. Then Bi<sub>2</sub>O<sub>3</sub> (4N), which has limited solubility in this temperature range, was introduced into the melt. It is necessary to hold the flux at the highest temperature (290°C) for 5–6 hours till it is fully saturated with bismuth oxide. The Bi<sub>2</sub>O<sub>3</sub> (~ 2–3 g) excess at the bottom of crucible was used as a melt nutrient during the crystal growth process.

As a result of the high temperature and flux activity, crucible corrosion strongly changes the rheological properties of the system. This corrosion of teflon crucibles leads to their mass losses by 0.6–2 g per growth run depending on flux temperature. One can see a significantly thinner crucible wall which has been in contact with the melt for approximately 10 days of the process duration. Besides, initial experiments showed that a fine suspension of metallic bismuth particles formed in the flux melt according to the

possible reaction:



This reaction leads to unwanted adhesion of these particles to the surface of the growing crystal and the depletion of Bi<sub>2</sub>O<sub>3</sub> in the flux. To prevent this process, KNO<sub>3</sub> (4N) was added to the flux at the final stage of its preparation. With this change, corrosion of the crucible does not lead to a change in the concentration of bismuth oxide in the melt. The following reaction is proposed to understand the chemistry taking place in the melt:



For subsequent experiments, a platinum crystal holder with a BaBiO<sub>3</sub> single crystal attached as a seed was immersed in the as-prepared flux melt. The seed was fixed to the holder with teflon tape and the same tape was used to insulate the contact between the seed and crystal holder as well as the part of the crystal holder immersed in the liquid. This seed mount makes it possible to carry on the electrochemical process on a surface of the seed of known geometry. The seed and the holder together served as the positive electrode. A metallic bismuth rod 4 mm in diameter was used as the cathode. The same bar was employed to check the electrochemical potential of the BKBO crystal growth process as a pseudo-reference electrode. To prevent the growth of parasitic crystals on the seed and to provide efficient stirring of the melt, a reciprocal vertical motion of the holder was employed with a frequency of 5 Hz. When the seed and melt reached an equilibrium temperature, the anode current was delivered to it at an average current density of ~ 2–3 mA/cm<sup>2</sup>. The subsequent crystal growth was performed at  $J = 0.3\text{--}0.5\text{ mA/cm}^2$  making assumptions concerning the varying area of the crystal surface. Thus, for the crystal with final dimensions of 15 × 12 × 6 mm<sup>3</sup>, the DC current value was increased at a rate of  $2 \times 10^{-3}\text{ mA/h}$  with constant average density 0.4 mA/cm<sup>2</sup>.

As has been pointed out, in a prolonged growth procedure, the physical-chemical parameters of the melt are varying due to corrosion of the teflon

Table 1

The main characteristics of the growth process of the  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  single crystals during 100 h

Process parameters	Growth method		
	Spontaneous crystallisation $x = 0.35\text{--}0.45$	Growth on a seed	
		$x = 0.4$	$x = 0.15$
BaO concentration, mol/mol KOH	0.014	0.009	0.045
$\text{Bi}_2\text{O}_3$ concentration in the melt	Below saturated	Saturated	Saturated
$\text{KNO}_3$ concentration, mol/mol KOH	—	0.002	0.01
Temperature of the flux-melt, °C	250	250	290
Current density, $\text{mA}/\text{cm}^2$	9–25 <sup>a</sup>	0.4	0.3
Growth rate of the (100) face, $\mu/\text{h}$	70 $\text{mm}^{3b}$	2.0	2.5
Reduction BaO concentration in the flux-melt for a synthesis run, %	58	8 <sup>c</sup>	2 <sup>c</sup>

<sup>a</sup>Calculated for the Pt anode or substrate area value.<sup>b</sup>Maximum volume of the separated single crystal.<sup>c</sup>For single crystals of more than 1  $\text{cm}^3$  in volume.

crucible, vaporization of water, and consumption of solute. For these reasons, the growth procedure was discontinued every 70–100 h to renew the melt. After the BKBO layer on  $\text{BaBiO}_3$  seed surface had reached an order 1–1.5 mm thickness, it was cut off. The crystal wafer treated with both chemical and mechanical polishing on a rotated disc covered with a fabric was steadily wetted by a HCl (35 wt%) water solution. Then it was washed off in distilled water and ethanol. The plate thus obtained was used as a secondary seed to grow a neutron-sized single crystal. Representative parameters for BKBO growth on seeds in comparison with those reported for experiments under spontaneous nucleation conditions are summarised in Table 1.

## 2.2. Growth morphology and microstructure of the BKBO crystals

A visual inspection of a number of the as-grown crystals shows that the single crystal surface formation occurs in the form of growing layers, that are packed close to the (1 0 0) face orientation, from the crystal fastening place towards its down part. The creep rate of the growth layers front across a parallel to the seed surface varies from 20 to 40  $\mu\text{m}/\text{h}$ . The growth rate in a perpendicular direction is an order of magnitude less. The BKBO single crystals

with potassium concentration close to  $x = 0.4$  present a cube-like habit (Fig. 1a.). In contrast, crystals with potassium concentration less than  $x = 0.2$  reveal extra (1 1 1)-type faces. Thus crystals at growth temperatures above 280°C acquire the shape of a cubeoctahedron (Fig. 1b.). At lower temperatures, crystals with low potassium content do not exhibit well-developed (1 1 1) faces and have high mosaicity of structure with the FWHM of the Bragg reflection curves up to 10°. This change of morphology and the extra high mosaicity crystal can probably be explained in terms of the  $T$ - $x$  phase diagram [12]. As can be seen in this case, the crystals grow in the temperature range corresponding to the phase transition from the rhombohedral R3 to orthorhombic  $\text{Ibmm}$  phase and may be phase separated during the growth process. It should be mentioned that the BKBO crystals with size up to 2.0  $\text{cm}^3$  are grown in quasi equilibrium conditions as demonstrated by Bragg reflection curves with FWHM not exceeding 1° regardless of potassium content.

## 2.3. Magnetic measurements and results

One of the most interesting and fundamental questions concerning the vortex structures in superconductors is the symmetry of the structure,



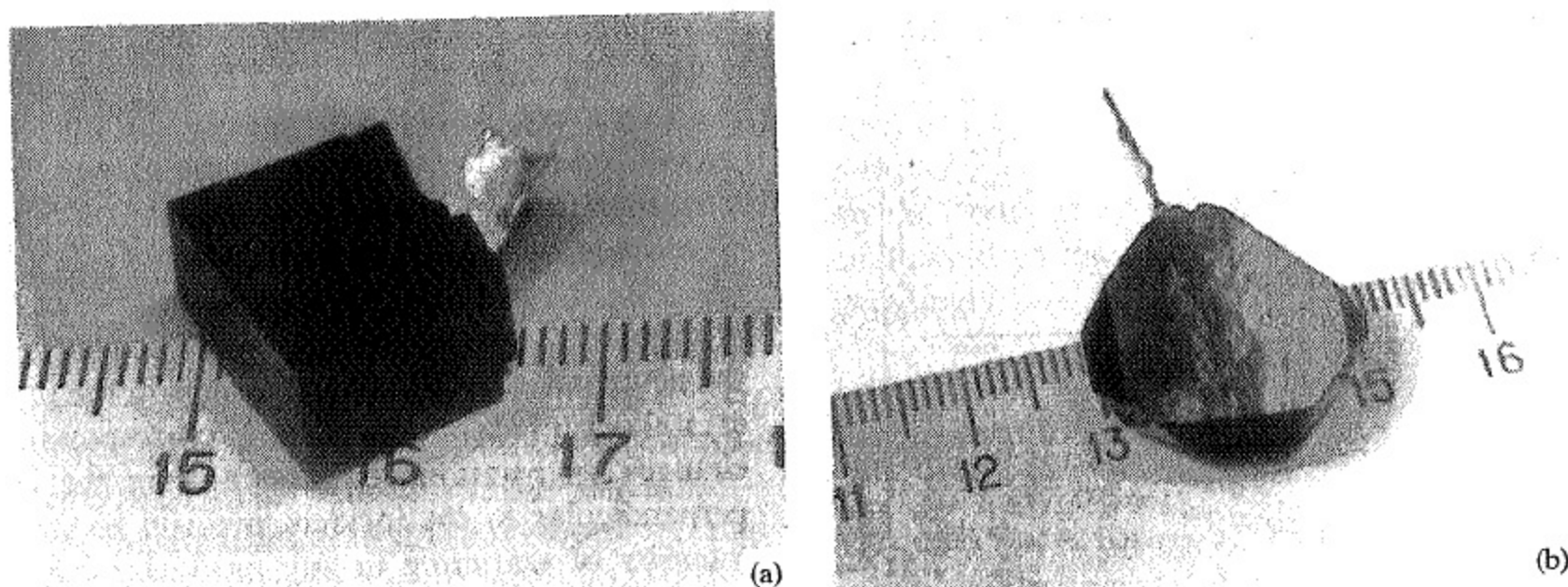


Fig. 1. The as-grown single crystals of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ : (a)  $x = 0.4$ ; (b)  $x < 0.2$ .

and whether or not they undergo a melting transition. The as-grown high-quality BKBO single crystal ( $x = 0.4$ ), weighing approximately 6 g, was employed in the SANS experiments using a NG-3 spectrometer at the NIST Center for Neutron Research. The experimental setup employed an electromagnet ( $H \leq 0.5$  T) and a cryostat ( $T \geq 4.5$  K) placed between the pole pieces. The magnetic field applied was approximately parallel to the incident and excited neutrons, while the crystal was oriented so that the field direction coincides with the cube edge. The beam diameter was 1 cm. Both isothermal and isofield scans were performed. Upon subtracting the background taken at zero field from the data observed at 2 kOe a pattern of Bragg peaks for the magnetic vortices lattice appears, revealing that an approximately six-fold symmetry has been obtained. There are several types of information that can be obtained from the data. The radial position of the peaks is directly related to the vortex flux quantum and the density of flux lines in the sample. Thus with increasing applied field the peak positions spread out from the beam centre as  $(B)^{1/2}$ . The widths of the peaks can also be obtained in both the radial and transverse (angular) directions, and the intensity can be monitored, all as a function of  $(H, T)$ . The integrated intensity of the vortex scattering as a function of temperature was also measured. The data demonstrate that the scattering intensity changes smoothly and continuously with temperature. In particular, we do not

observe any discontinuous behaviour such as might be expected in the first-order melting transition of vortices lattice. The study of BKBO vortex lattice pattern and its transforming under higher fields are currently under the process and will be published elsewhere.

The sample with a cube shape for SQUID measurements was cut from the large single crystal part in such a way that all the faces corresponded to the (1 0 0)-type planes. One of the faces is the growth face. The magnetisation hysteresis loops at liquid helium temperature and various orientation  $H$  with respect to the natural crystal face are given in Fig. 2. When the magnetic field was applied perpendicularly to the growth surface of a single crystal, a greater hysteresis loop scale was noted than at the field applied parallel to it. Besides, the shift of the peak-effect field has been pointed out. At temperatures of the order of 3 K this field along the perpendicular direction equals 20 kOe, whereas in the parallel direction – 13 kOe. Anisotropic character of isotherms of the reduced vortices pinning force has been found, which determines the type of pinning centres in the second-type superconductors. The anisotropy of the indicated anomalies for isotropic single crystals with the perovskite structure is likely to be connected with the peculiarities of layered growth. Furthermore, in the electrochemical growth conditions defects ordering under the influence of the applied electric field becomes possible. We have tried to find factors which may

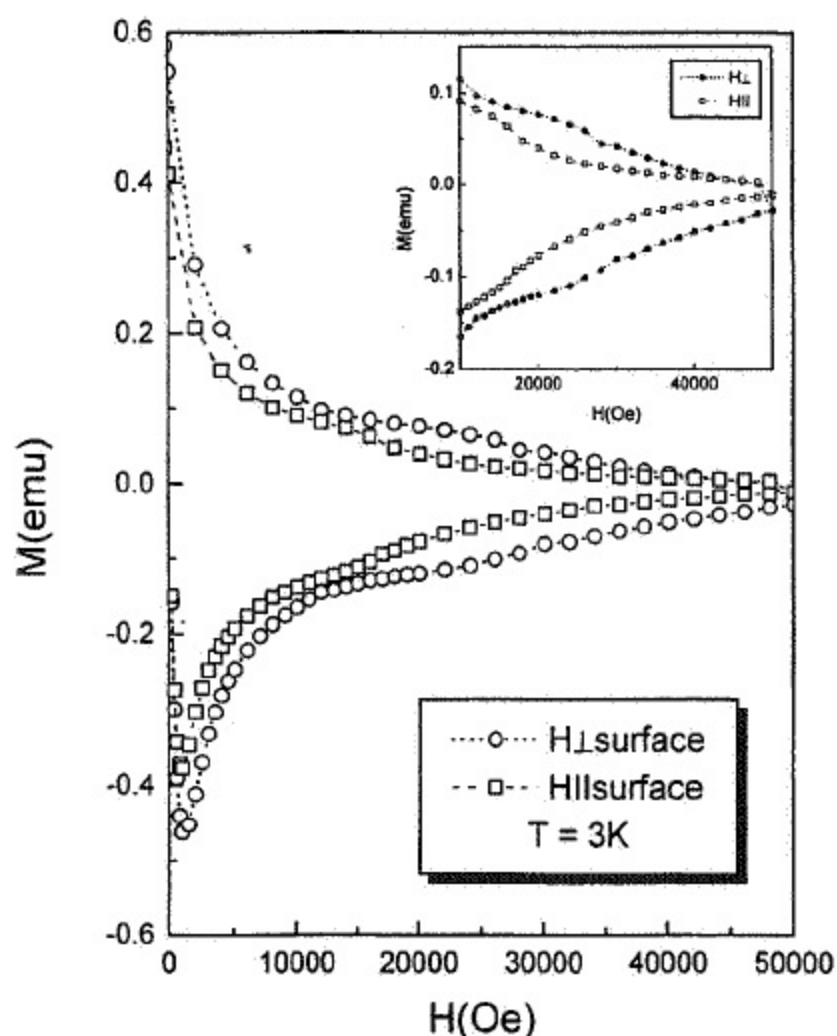


Fig. 2. The magnetisation hysteresis loops of  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  single crystal at  $T = 3\text{ K}$  depending on various applied field orientation with respect to the natural crystal surface.

be responsible for the anisotropy of pinning force in our crystals. For this reason we have measured the SANS patterns at two different orientations of the crystal (rotated to  $90^\circ$ ) in the plane perpendicular to the neutron beam (Fig. 3). The measurements were made at the neutron wave length of  $12\text{ \AA}$ , with a 2D-SANS detector moved to the distance of  $12\text{ m}$  at room temperature. The square-shaped pattern of the neutron scattering has its corners in the  $[1\ 1\ 0]$  crystallographic direction and, correspondingly, changes on rotation of the sample in the plane perpendicular to the incident neutron beam. The intensity of scattering in any particular direction falls off by the law of  $1/Q^4$ . This scattering of the Porod-type is evidence that the defects caused by the crystal growth technique used are considerably larger than the wave length range explored. This fact agrees with the picture of defects alternating with periods of approximately  $1\text{--}2\text{ }\mu\text{m}$  seen with a polarisation microscope on the crystal cut perpendicular to the growth layers after selective etching. The problem can be explained on the basis of the growth mechanism investigations and leads to the determination of the influence of growth defects on vortices lattice pinning and critical parameters of high  $T_c$  superconductors related to it.

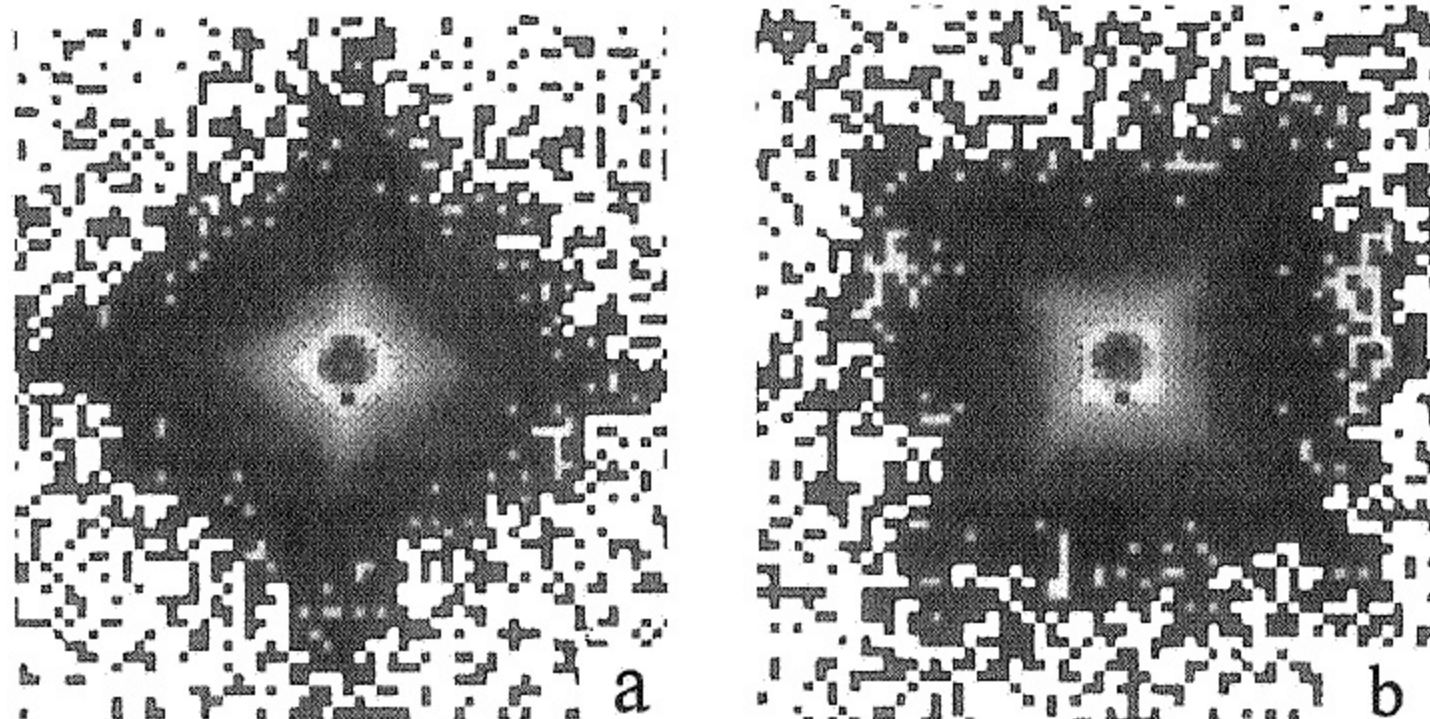


Fig. 3. The SANS patterns at two different orientations of the crystal, (b) rotated to  $90^\circ$  about (a), in the plane perpendicular to the neutron beam.

### 3. Conclusions

Single crystals of BKBO up to 2 cm<sup>3</sup> in size with the FWHM of the Bragg reflection curves not exceeding 1° have been grown for the first time by a seeded growth method. The optimal growth rate of the (1 0 0) crystal face reaches 2–4 µm/h. The morphology features and crystals habit vary with the decreasing potassium content, from nearly a cube at  $x = 0.4$  to cubeoctahedron shape containing extra (1 1 1)-type faces at  $x < 0.2$ . The anisotropy of magnetization hysteresis loops of the Ba<sub>0.6</sub>K<sub>0.4</sub>BiO<sub>3</sub> superconductor depending on the external magnetic fields orientation with respect to the natural growth surface of the single crystal was caused by the electrochemical growth induced defects in the crystal volume. Using the small-angle neutron scattering method we have first restored the pattern of the vortex lattice structure in the BKBO superconductor. The smooth character of the intensity of magnetic scattering variation near the critical temperature and magnetic field has been found.

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